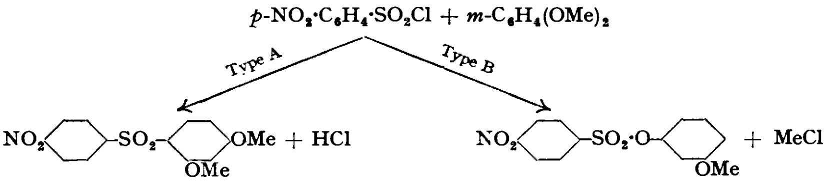
5. *The Reaction between Sulphonyl Chlorides and Dimethoxybenzenes in the Presence of Zinc Chloride.*

By Harold Burton and Eric Hoggarth.

Alkyl- and aryl-sulphonyl chlorides react with the dimethoxybenzenes in the presence of zinc chloride, giving the corresponding anisyl alkyl- and aryl-sulphonates and, in some cases, the dimethoxyphenylarylsulphones. In general, formation of the sulphonate is favoured by the *o*- and *p*-dimethoxybenzenes and by the more reactive sulphonyl chlorides.

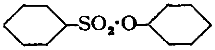
The preparation of a series of diaryl- and arylalkyl-sulphones containing hydroxyl, methoxyl, and amino-groups was undertaken in order that the antibacterial activities of compounds related to the very active 4 : 4′-diaminodiphenylsulphone might be determined. It was discovered that *p*-nitrobenzenesulphonyl chloride and resorcinol dimethyl ether reacted vigorously in the presence of zinc chloride at 125°, and the main product was proved by independent synthesis to be 4-*nitro*-2′ : 4′-*dimethoxydiphenylsulphone* (I) (Type A). A second compound (II), $C_{13}H_{11}O_6NS$, was also isolated from the reaction mixture; at higher temperatures this substance preponderated. The possibility that (II) was 4-nitro-2′(or 4′)-hydroxy-4′(or 2′)-methoxydiphenylsulphone, arising by the demethylation of (I), was unlikely owing to its insolubility in alkali hydroxide. After it had been established that methyl chloride was liberated during the reaction, it appeared certain that (II) was actually m-*anisyl* p-*nitrobenzenesulphonate* (Type B); this was confirmed by independent synthesis.

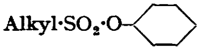


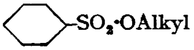
(I.) (II.)

The scope of the method was then assessed by investigating the reaction between the three dimethoxybenzenes and various alkyl- and aryl-sulphonyl chlorides. In general, type B reaction is more common than type A, particularly with the alkylsulphonyl chlorides: but in some cases, as above and with, for example, veratrole and arylsulphonyl chlorides, both types occur simultaneously. The point of attack in the dimethoxybenzene molecule thus seems to depend on the nature of both the sulphonyl chloride and the dimethoxybenzene; no true generalisation has been found possible.

The case of 3-methyl-*n*-butanesulphonyl chloride and the dimethoxybenzenes was complicated by the difficulty of characterising the oily products; the sulphones were therefore demethylated, and the crystalline hydroxy-compounds obtained. Unexpectedly it was found that the sulphonates were sufficiently stable to be demethylated by boiling 46% hydrobromic acid and it was thus possible to prepare corresponding crystalline compounds from them also. Alkali, however, hydrolysed the sulphonates to the corresponding phenols and this was used as additional proof of constitutions. It is remarkable that sulphonates of types (III) and (IV) are stable, whereas an example of type (V) is reported by Walter (*J. Amer. Chem. Soc.*, 1943, **65**, 739) to be very unstable.


(III.)


(IV.)


(V.)

It has been observed that a number of compounds of type (III) containing nitro-groups are strongly discoloured on standing in the light.

The reactions were carried out in an apparatus similar to that used for methoxy-determinations by Zeisel's method, and the liberated methyl chloride collected in a trap, cooled in solid carbon dioxide and ethyl alcohol. In instances where type A reactions preponderated, a little methyl chloride was condensed but much hydrogen chloride was found in the effluent gas. In examples of type B reactions the amount of methyl chloride corresponded to 60—75% of the theoretical and in those cases in which both sulphonate and sulphone were isolated the amount of methyl chloride was roughly proportional to the amount of sulphonate. No reaction was detected when the dimethoxybenzenes were heated with zinc chloride alone, or with the sulphonyl chlorides alone, and the starting materials were recovered unchanged in all instances after prolonged heating at 20—30° above the usual reaction temperature.

The compounds were tested for antibacterial activity by Dr. Martin of the Biological Department, Imperial Chemical Industries Limited. Blackley. No high degree of activity was found in any instance.

EXPERIMENTAL.

I. *Reactions with Arylsulphonyl Chlorides.*

4-*Nitro*-2′ : 4′-*dimethoxydiphenylsulphone* (I).—(*a*) *p*-Nitrobenzenesulphonyl chloride (44 g.) and resorcinol dimethyl ether (28 g.) were melted together, freshly crushed zinc chloride (41 g.) added, and the mixture slowly heated in a slow stream of dry nitrogen. At 98° (internal temperature) a deep red coloration was observed, at 106° some hydrogen chloride escaped, and at 125° evolution of gas was rapid. Heating was continued for 30 mins. at 125°, during which time a small amount of methyl chloride (0·8 g.) was condensed in the solid carbon dioxide trap. The reaction mixture was cooled and extracted with boiling benzene (500 c.c.), and the extract washed with 5% sodium hydroxide solution, then with water, and evaporated. 4-*Nitro*-2′ : 4′-*dimethoxydiphenylsulphone* crystallised from β-ethoxyethyl alcohol in colourless prisms, m. p. 183° (7·8 g.; 12·0%) (Found: C, 51·6; H, 3·8. $C_{14}H_{13}O_6NS$ reuires C, 52·0; H, 4·0%).

(*b*) To a solution of sodium (0·25 g.) in absolute ethyl alcohol (100 c.c.) was added 2 : 4-dimethoxythiophenol (1·7 g.), followed by *p*-chloronitrobenzene (1·7 g.), and the mixture refluxed for 3 hours. Water (150 c.c.) was added, and the solid collected, washed with water, and crystallised from ethyl alcohol, giving lustrous needles of 4-*nitro*-2′ : 4′-*dimethoxydiphenyl sulphide* (2·1 g.; 75·6%), m. p. 126° (Found: C, 57·7; H, 4·0. $C_{14}H_{13}O_4NS$ requires C, 57·7; H, 4·4%). This sulphide (2·0 g.) in acetic acid (10 c.c.) was heated to boiling under reflux, and 30% hydrogen peroxide (3·0 c.c.) added. When the reaction subsided, the solution was warmed on the water-bath for 1 hr. and diluted with water (300 c.c.), and the solid collected. From ethyl alcohol, colourless plates, m. p. 183°, undepressed by admixture with the compound obtained under (*a*), were obtained (1·8 g.; 81·1%) (Found: C, 51·7; H, 4·1%).

4-*Amino*-2′ : 4′-*dimethoxydiphenylsulphone*.—The above sulphone (6·5 g.) was reduced with hydrogen in presence of Raney nickel (absorption, corrected to N.T.P., 1375 c.c. Calc., 1352 c.c.). The filtered solution was evaporated; the residue crystallised from ethyl alcohol in long colourless needles (4·5 g.; 76·8%), m. p. 196—198° (Found: C, 57·05; H, 5·0. $C_{14}H_{15}O_4NS$ requires C, 57·3; H, 5·2%).

m-*Anisyl* p-*Nitrobenzenesulphonate* (II).—(*a*) When *p*-nitrobenzenesulphonyl chloride (22 g.), resorcinol dimethyl ether (14 g.), and zinc chloride (41 g.) were quickly heated in an oil-bath at 135—140°, a vigorous reaction with much charring took place. The *ester*, isolated as described under (I) (*a*), had m. p. 109° (from β-ethoxyethyl alcohol, in which it was markedly more soluble than 4-nitro-2′ : 4′-dimethoxydiphenylsulphone) (3·2 g.; 10·3%) (Found: C, 50·6; H, 3·75; N, 4·45. $C_{13}H_{11}O_6NS$ requires C, 50·5; H, 3·6; N, 4·5%). This compound (1·5 g.) was refluxed with potassium hydroxide (0·8 g.) in water (15 c.c.) and dioxan (5 c.c.) for 5 hours, the clear liquid evaporated under reduced pressure, the residue dissolved in water (30 c.c.), filtered (charcoal), and made acid to Congo-red paper (concentrated hydrochloric acid), and the oil extracted with ether. The residue left on evaporation of the dried extracts was distilled, giving a colourless oil (0·5 g.; 80%), b. p. 120—125°/15 mm., which was identified by conversion into 2 : 4 : 6-tribromo-3-methoxyphenol, m. p. 103°, not depressed by an authentic sample.

(*b*) A solution of resorcinol monomethyl ether (6·2 g.) in dry pyridine (30 c.c.) was shaken with *p*-nitrobenzenesulphonyl chloride (11·1 g.). The mixture, which became warm (70—75°), was kept overnight and then treated with water (100 c.c.), and the solid collected and washed with water. From β-ethoxyethyl alcohol, colourless prisms, m. p. 109°, not depressed by the compound from (*a*), were obtained (8·2 g.; 52·6%) (Found: C, 50·8; H, 3·7%).

m-*Anisyl Sulphanilate*.—The nitrobenzenesulphonate (3·1 g.) was reduced (hydrogen and Raney nickel catalyst; absorption, reduced to N.T.P., 720 c.c.; calc., 672 c.c.). The *amino*-compound crystallised from benzene–light petroleum (b. p. 60—80°) in colourless prisms (2·2 g.; 78·8%), m. p. 37—38° (Found: C, 56·2; H, 5·05. $C_{13}H_{13}O_4NS$ requires C, 55·9; H, 4·7%).

p-*Anisyl* p-*Nitrobenzenesulphonate*.—The reaction between quinol dimethyl ether and *p*-nitrobenzenesulphonyl chloride in the presence of zinc chloride as described above gave as the principal isolated product this *ester* (15·5%), m. p. 153—154° (colourless prisms from ethyl alcohol). Methyl chloride (55% of the theoretical amount) was also obtained. By the reaction between quinol monomethyl ether and *p*-nitrobenzenesulphonyl chloride in pyridine solution, the same compound was obtained (59%), m. p. 153—154°, not depressed by the compound obtained by the first route (Found: S, 10·4. $C_{13}H_{11}O_6NS$ requires S, 10·35%).

p-*Anisyl Sulphanilate*.—The above compound (3·1 g.) was reduced in methyl alcohol with Raney nickel (absorption 650 c.c., calc. 672 c.c., at N.T.P.), and the filtered solution concentrated. The *amino*-compound separated, on cooling, in colourless needles (2·4 g.; 86%), m. p. 168° (Found: C, 56·05; H, 4·75%).

o-*Anisyl* p-*Nitrobenzenesulphonate*.—Veratrole and *p*-nitrobenzenesulphonyl chloride, in the presence of zinc chloride, gave as the main isolated product this *ester* (15·6%), m. p. 112° (from ethyl alcohol). Methyl chloride (58%) was also obtained. Reaction of guaiacol and *p*-nitrobenzenesulphonyl chloride in pyridine gave the same compound (88%), m. p. 112°, not depressed by the compound obtained by the first route (Found: S, 10·1 $C_{13}H_{11}O_6NS$ requires S, 10·35%).

o-*Anisyl Sulphanilate*.—The above nitro-compound was reduced in the usual manner (76·1%); the *amine* crystallised from methyl alcohol (in which it was very soluble) in colourless prisms, m. p. 141—142° (Found: C, 55·5; H, 4·75%).

Reaction of m-*Nitrobenzenesulphonyl Chloride with Dimethoxybenzenes*.—In these cases the only product isolated was the sulphonate and identity of the product with that prepared from the monomethyl ether of the corresponding dihydroxybenzene was established by mixed m. p. and by reduction to identical amino-compounds: p-*Anisyl* m-*nitrobenzenesulphonate*, m. p. 91—92° (Found: C, 50·9; H, 3·8; S, 10·1%); p-*anisyl* m-*aminobenzenesulphonate*, m. p. 62° (Found: C, 55·4; H, 4·3%). m-*Anisyl* m-*nitrobenzenesulphonate*, m. p. 71—72° (Found: C, 50·65; H, 3·9%); m-*anisyl* m-*aminobenzenesulphonate*, oil (Found: C, 56·3; H, 5·15%) [*acetyl* derivative, m. p. 87° (Found: N, 4·5; S, 9·85. $C_{15}H_{15}O_5NS$ requires N, 4·4; S, 10·0%)]. o-*Anisyl* m-*nitrobenzenesulphonate*, m. p. 84° (Found: C, 50·3; H, 3·55; S, 10·15%); o-*anisyl* m-*aminobenenzesulphonate*, m. p. 110° (Found: C, 55·75; H, 4·5%).

2 : 4 : 4′-*Trimethoxydiphenylsulphone*.—Anisole-*p*-sulphonyl chloride (10·3 g.), resorcinol dimethyl ether (6·9 g.), and zinc chloride (6·8 g.) reacted at 110° with evolution of much hydrogen chloride but only a trace of methyl chloride. The product was extracted several times with chloroform–ether, and the extracts evaporated to 200 c.c., filtered, washed successively with dilute hydrochloric acid, water, dilute sodium hydroxide solution, and water, and evaporated. The residue crystallised from methyl alcohol in colourless prisms (8·2 g.; 53·2%), m. p. 118°. Repeated crystallisation from methyl alcohol raised the m. p. to 123° (Found: C, 58·2; H, 5·2; S, 10·6. $C_{15}H_{16}O_5S$ requires C, 58·4; H, 5·2; S, 10·4%).

m-*Anisyl* p-*Methoxybenzenesulphonate*.—The sulphonyl chloride reacted with resorcinol monomethyl ether in pyridine solution to give the *ester*, b. p. 200—202°/0·5 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5731, which slowly set to a crystalline solid; this, recrystallised from methyl alcohol, formed colourless prisms (88%), m. p. 52° (Found: C, 56·9; H, 4·6. $C_{14}H_{14}O_5S$ requires C, 57·15; H, 4·8%).

4-*Chloro*-2′ : 4′-*dimethoxydiphenylsulphone*.—This *compound*, obtained in 54·6% yield by interaction of *p*-chlorobenzenesulphonyl chloride and resorcinol dimethyl ether as described under 2 : 4 : 4′-trimethoxydiphenylsulphone, crystallised from alcohol in colourless prisms, m. p. 166° (Found: C, 54·1; H, 4·25. $C_{14}H_{13}O_4ClS$ requires C, 53·75; H, 4·2%).

m-*Anisyl* p-*Chlorobenzenesulphonate*.—*p*-Chlorobenzenesulphonyl chloride and resorcinol monomethyl ether reacted in pyridine solution to give the *ester* (58%), b. p. 190—191°/0·5 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5788, which did not solidify (Found: C, 52·2; H, 3·8. $C_{13}H_{11}O_4ClS$ requires C, 52·3; H, 3·7%).

2 : 4-*Dimethoxydiphenylsulphone*, obtained from benzenesulphonyl chloride and resorcinol dimethyl ether by the procedure given under 2 : 4 : 4′-trimethoxydiphenylsulphone, formed colourless prisms (44%), m. p. 121—122°, from ethyl alcohol (Found: C, 60·5; H, 5·2; S, 11·6. $C_{14}H_{14}O_4S$ requires C, 60·4; H, 5·0; S, 11·5%). Demethylation with 46% hydrobromic acid gave 2 : 4-dihydroxydiphenylsulphone, m. p. 121° (U.S.P. 2,288,282; *Chem. Abs.*, 1943, **37**, 141, gives m. p. 115—116°) (Found: C, 54·25, 53·7; H, 4·4, 4·1. Calc. for $C_{12}H_{10}O_4S,H_2O$: C, 53·7; H, 4·5%).

m-*Anisyl benzenesulphonate*, obtained from resorcinol monomethyl ether and benzenesulphonyl chloride, was a colourless oil, b. p. 188—190°/1·0 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5636 (Found: S, 12·0. $C_{13}H_{12}O_4S$ requires S, 12·1%).

Reaction of Benzenesulphonyl Chloride and Toluene-p-*sulphonyl Chloride with Veratrole*.—Two compounds were formed in each case and by comparison with the sulphonates obtained from guaiacol in pyridine solution one member of each pair was identified as the *o*-anisyl arylsulphonate. The excluded member of each pair is regarded by analogy as the 3 : 4-dimethoxy-sulphone. In the case of 3 : 4-dimethoxydiphenylsulphone the reaction mixture was best hydrolysed with alkali hydroxide, and the sulphone then extracted with chloroform. The following were obtained: 3 : 4-*Dimethoxydiphenylsulphone*, m. p. 118—119° (Found: C, 60·5; H, 5·2. $C_{14}H_{14}O_4S$ requires C, 60·4; H, 5·0%). o-*Anisyl benzenesulphonate*, m. p. 51—52° (Found: C, 59·15; H, 4·8. $C_{13}H_{12}O_4S$ requires C, 59·1; H, 4·5%). 3 : 4-*Dimethoxy*-4′-*methyldiphenylsulphone*, m. p. 130—131° (Found: C, 61·4; H, 5·5. $C_{15}H_{16}O_4S$ requires C, 61·6; H, 5·5%). o-*Anisyl* p-*toluenesulphonate*, m. p. 85—86° (Found: C, 60·5; H, 4·65. $C_{14}H_{14}O_4S$ requires C, 60·4; H, 5·0%).

Reaction between *o*-nitrobenzenesulphonyl chloride and the dimethoxybenzenes proceeded in an uncontrolled manner and charred products were obtained.

II. *Reactions with Alkylsulphonyl Chlorides.*

p-*Anisyl* 3-*Methyl*-n-*butanesulphonate*.—(*a*) Quinol dimethyl ether (6·9 g.), 3-methyl-*n*-butanesulphonyl chloride (8·6 g.), and anhydrous zinc chloride (6·8 g.) were heated slowly in a stream of dry nitrogen. At 92° (internal temperature) a blue coloration was observed, at 102° some methyl chloride condensed in the solid carbon dioxide trap, and at 125° condensation of methyl chloride was rapid and continued for about 15 mins. After being heated for a further 15 mins. at 125°, the mixture was cooled and dissolved in ether (400 c.c.). The solution was shaken successively with dilute hydrochloric acid (20 c.c. of conc. acid and 100 c.c. of water), water, 5% sodium hydroxide solution, and water, dried, and evaporated. The residue was distilled, giving a main fraction (7·5 g.; 58·1%), b. p. 150—155°/0·1 mm., which on redistillation gave a colourless oil, b. p. 150—151°/0·1 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5112 (Found: C, 56·1; H, 7·2. $C_{12}H_{18}O_4S$ requires C, 55·8; H, 7·0%). The yield of methyl chloride was 1·8 g. (71·3%), but no fuming due to hydrogen chloride was noticed. The above sulphonate (2·6 g.) was boiled with sodium hydroxide (1 g.) in water (15 c.c.) and dioxan (5 c.c.) for 7 hrs., the clear liquid evaporated under reduced pressure, and the residue dissolved in water (30 c.c.), filtered (charcoal), made acid (Congo-red) (concentrated hydrochloric acid), and extracted with ether. Distillation gave a colourless oil, b. p. 120—130°/15 mm., setting to a mass of colourless crystals (1·1 g.; 88·7%), m. p. 48°. Plates were obtained from light petroleum containing a little ethyl acetate, m. p. 53°, not depressed by authentic quinol monomethyl ether.

(*b*) A solution of quinol monomethyl ether (15·5 g.) in dry pyridine (20 c.c.) was treated with 3-methyl-*n*-butanesulphonyl chloride (21·3 g.) and kept for 24 hours. The mixture was ground with water (100 c.c.), concentrated hydrochloric acid added (Congo-red), the oil extracted with carbon tetrachloride, and the extract washed with 10% sodium hydroxide solution, then with water, and evaporated. Distillation gave a colourless oil (24 g.; 74·5%), b. p. 148—150°/0·1 mm., $n_D^{20^\circ}$ 1·5109 (Found: C, 55·95; H, 7·3%). Hydrolysis as described under (*a*) gave quinol monomethyl ether (80%).

p-*Hydroxyphenyl* 3-*Methyl*-n-*butanesulphonate.*—*p*-Anisyl 3-methyl-*n*-butanesulphonate (5·2 g.) was heated with 48% hydrobromic acid (50 c.c.) just below the b. p. with mechanical stirring for 16 hours. The liquid was cooled, and ice (200 g.) added, followed by 30% sodium hydroxide solution (70 c.c.). The alkaline solution was extracted several times with small amounts of benzene, and the aqueous layer stirred with charcoal, filtered, and made acid to Congo-red paper with concentrated hydrochloric acid. The liberated p-*hydroxyphenyl* ester was extracted with benzene, dried, and distilled, giving a pale yellow oil, b. p. 185—188°/0·5 mm., $n_D^{20^\circ}$ 1·5220 (Found: C, 53·9; H, 6·7. $C_{11}H_{16}O_4S$ requires C, 54·1; H, 6·6%).

Hydrolysis of this compound (1·1 g.) gave quinol (0·3 g.), m. p. 166—168°, which was converted into its diacetate, plates from dilute acetic acid, m. p. 121°, not depressed by an authentic sample.

Acetylation of the *p*-hydroxylphenyl ester (0·75 g.) with acetic anhydride (3 c.c.) and 1 drop of concentrated sulphuric acid gave p-*acetoxyphenyl* 3-*methyl*-n-*butanesulphonate*, which, crystallised from light petroleum, gave colourless plates (0·3 g.), m. p. 48° (Found: C, 54·2; H, 6·5. $C_{13}H_{18}O_5S$ requires C, 54·5; H, 6·3%).

Quinol Bis-3-*methyl*-n-*butanesulphonate.*—The *p*-hydroxyphenyl ester (2·4 g.) in pyridine (2 c.c.) was treated with 3-methyl-*n*-butanesulphonyl chloride (1·7 g.). After 48 hrs., the mixture was treated with water (100 c.c.), and the solid collected and crystallised from methyl alcohol, giving colourless prisms (2·0 g.; 53%), m. p. 61° (Found: C, 50·5; H, 6·8. $C_{16}H_{26}O_6S_2$ requires C, 50·8; H, 6·9%).

Quinol (11 g.) in pyridine (30 c.c.) was treated (stirring) with 3-methyl-*n*-butanesulphonyl chloride (34 g.), the temperature being controlled by external cooling (ice). After 18 hours, the mixture was treated with water (200 c.c.) and made strongly alkaline with 20% sodium hydroxide solution. Quinol bis-3-methyl-*n*-butanesulphonate was collected, washed with water, and crystallised from methyl alcohol, giving large colourless plates (10·1 g.; 26·7%), m. p. 61°. The alkaline filtrate was acidified (hydrochloric acid), the oil extracted with carbon tetrachloride, and the solvent evaporated. The residual oil was distilled, giving a small amount of unchanged quinol and a main fraction, b. p. 175—185°/0·5 mm., from which was obtained by redistillation pure *p*-hydroxyphenyl 3-methyl-*n*-butanesulphonate (6·3 g.; 25·8%), b. p. 180—182°/0·5 mm., $n_D^{20^\circ}$ 1·5219 (Found: C, 54·4; H, 6·7%). The acetoxy-compound prepared from this had m. p. 48°, undepressed by specimens prepared by the other methods.

2 : 5-*Dimethoxythiophenol.*—This *compound* was prepared by Suter and Johnson's method (*J. Amer. Chem. Soc.*, 1932, **54**, 4102), in 48% yield, as a colourless oil, b. p. 138—140°/20 mm., $n_D^{20^\circ}$ 1·5848 (Found: S, 18·7. $C_8H_{10}O_2S$ requires S, 18·8%).

2 : 5-*Dimethoxyphenyl* iso*Amyl Sulphide.*—Sodium (2·8 g.) in absolute ethyl alcohol was treated with the above thiophenol (17 g.), and *iso*amyl bromide (18 g.) added down a reflux condenser with shaking. A vigorous reaction took place which was completed on the steam-bath (3 hrs.). The mixture was diluted with water and ice, and the solid collected and washed with ice-water (yield, 21 g.; 87·5%). A small specimen was distilled, b. p. 153—155°/0·5 mm., and set to a crystalline mass, m. p. 31—33° (Found: S, 13·5. $C_{13}H_{20}O_2S$ requires S, 13·3%).

2 : 5-*Dimethoxyphenyl*iso*amylsulphone.*—The crude sulphide (20 g.) was dissolved in boiling acetic acid (75 c.c.), and 30% hydrogen peroxide (45 c.c.) added down a long reflux condenser. The reaction, at first violent, was completed on the steam-bath (2 hrs.), the liquor diluted with water (200 c.c.), and the oil extracted with benzene. The residue left after evaporation of the solvent was distilled, b. p. 198—198·5°/0·8 mm., $n_D^{20^\circ}$ 1·5290 (17·1 g.; 79·2%) (Found: C, 57·15; H, 7·1. $C_{13}H_{20}O_4S$ requires C, 57·35; H, 7·35%).

2 : 5-*Dihydroxyphenyl*iso*amylsulphone.*—The methoxy-sulphone (5·4 g.) and 46% hydrobromic acid (50 c.c.) were refluxed with stirring for 12 hours. The liquid was cooled (ice-salt bath) and stirred whilst concentrated sodium hydroxide solution was run in until alkaline (Clayton-yellow). The alkaline solution was extracted several times with carbon tetrachloride, cleared with charcoal, and made strongly acid (concentrated hydrochloric acid), and the oil extracted with benzene. The residue left on evaporation of the solvent was distilled, giving a pale yellow liquid, b. p. 195—196°/0·8 mm., $n_D^{20^\circ}$ 1·5499, which solidified on long standing to a crystalline mass (3·6 g.; 53·8%), m. p. 56° (Found: C, 53·8; H, 6·5. $C_{11}H_{16}O_4S$ requires C, 54·1; H, 6·6%). Acetylation with acetic anhydride and 1 drop of concentrated sulphuric acid gave colourless prisms of the *diacetate*, m. p. 97° (Found: C, 54·1; H, 6·1. $C_{15}H_{20}O_6S$ requires C, 54·9; H, 6·1%).

m-*Anisyl* 3-*Methyl*-n-*butanesulphonate.*—The reaction between 3-methyl-*n*-butanesulphonyl chloride and resorcinol dimethyl ether in the presence of zinc chloride gave m-*anisyl* 3-*methyl*-n-*butanesulphonate* (63·2%), b. p. 178—180°/0·1 mm., $n_D^{20^\circ}$ 1·5119 (Found: C, 55·7; H, 6·7. $C_{12}H_{18}O_4S$ requires C, 55·8; H, 7·0%). Methyl chloride (75%) was collected, and a deep red colour was produced in the reaction mixture.

The same compound was obtained (47%) from resorcinol monomethyl ether and 3-methyl-*n*-butanesulphonyl chloride in the presence of pyridine, b. p. 157—158°/0·05 mm., $n_D^{20^\circ}$ 1·5117 (Found: C, 56·05; H, 7·15%).

Both specimens of this compound were hydrolysed to resorcinol monomethyl ether, identified as its 2 : 4 : 6-tribromoderivative, m. p. 103°.

m-*Hydroxyphenyl* 3-*Methyl*-n-*butanesulphonate.*—This *compound*, obtained by demethylation of the *m*-anisyl ester as described under the *p*-hydroxy-ester, had b. p. 165—167°/0·1 mm., m. p. 48—50° (Found: C, 54·0, 54·5; H, 6·7, 6·6. $C_{11}H_{16}O_4S$ requires C, 54·1; H, 6·6%). The same compound was obtained (55%) by treating resorcinol with 3-methyl-*n*-butanesulphonyl chloride (1 mol.) in pyridine and had m. p. 48—50°, not depressed by specimens obtained by the former methods. Hydrolysis gave resorcinol (66%), identified by mixed m. p.

2 : 4-*Dimethoxyphenyl*iso*amylsulphone.*—This *compound*, prepared from 2 : 4-dimethoxythiophenol as described under 2 : 5-dimethoxyphenyl*iso*amylsulphone, had b. p. 172—173°/0·1 mm., $n_D^{20^\circ}$ 1·5508 (Found: C, 57·85; H, 7·2. $C_{13}H_{20}O_4S$ requires C, 57·35; H, 7·35%).

p-*Anisyl Methanesulphonate.*—(*a*) Quinol dimethyl ether (6·9 g.) and methanesulphonyl chloride (5·8 g.) reacted in the presence of zinc chloride (13·6 g.) to give methyl chloride (1·4 g.; 56%) and p-*anisyl methanesulphonate*, b. p. 180—185°/25 mm., crystallising in colourless prisms from aqueous ethyl alcohol, m. p. 79—80° (3·7 g.; 55·2%) (Found: C, 47·2; H, 5·15. $C_8H_{10}O_4S$ requires C, 47·5; H, 4·95%).

(*b*) Quinol monomethyl ether (6·2 g.) and methanesulphonyl chloride (6·3 g.) in pyridine (10 c.c.) gave colourless prisms (7·0 g.; 69%), m. p. 79—80°, not depressed by the compound prepared as in (*a*).

p-*Hydroxyphenyl Methanesulphonate.*—*p*-Anisyl methanesulphonate (4·0 g.) was demethylated by 46% hydrobromic acid (40 c.c.) as described for the 3-methyl-*n*-butanesulphonate, giving a colourless oil (3·2 g.; 66·5%), b. p. 172—174°/0·5 mm., which solidified to a crystalline mass, m. p. 68—70°. From benzene–light petroleum, colourless prisms, m. p. 73°, were obtained (Found: C, 44·5; H, 4·1. $C_7H_8O_4S$ requires C, 44·7; H, 4·3%).

Quinol Bismethanesulphonate.—*p*-Hydroxyphenyl methanesulphonate (1·9 g.) in pyridine (6 c.c.) with methanesulphonyl chloride (1·3 g.) gave colourless needles (1·65 g.; 62%), from ethyl alcohol, m. p. 168° (Found: C, 35·8; H, 3·6. $C_8H_{10}O_6S_2$ requires C, 36·1; H, 3·8%).

Quinol (5·5 g.) in pyridine (8 c.c.) with methanesulphonyl chloride (5·7 g.; 1 mol.), as described for the corresponding *iso*pentane compounds, gave *p*-hydroxyphenyl methanesulphonate (1·5 g.; 15·9%), m. p. 73° not depressed by the compound prepared by the former route, and quinol bismethanesulphonate (1·1 g.; 8·3%), m. p. 168°, also identical with the compound prepared as above.

2 : 5-*Dimethoxyphenylmethylsulphone.*—This *compound*, prepared as described for the *iso*amylsulphone, crystallised from alcohol in colourless prisms, m. p. 77°, depressed to 64° by admixture with *p*-anisyl methanesulphonate (Found : C, 49·6; H, 5·7. $C_9H_{12}O_4S$ requires C, 50·0; H, 5·6%).

THE UNIVERSITY, LEEDS, 2.
IMPERIAL CHEMICAL INDUSTRIES LIMITED, RESEARCH LABORATORIES,
BLACKLEY, MANCHESTER, 9.

[*Received, September* 12*th*, 1944.]